Analog Technology Corporation

A Study on the
Optimization of a Pyrolysis/Hydrogen
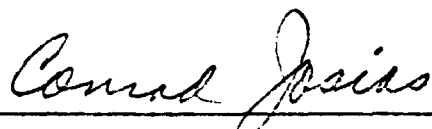Flame Detector System

FINAL REPORT

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ABSTRACT

Pyrolyzers, hydrogen flame detectors and supporting
gas systems were investigated as part of a continuing
program to develop a spaceworthy Pyrolysis/Hydrogen Flame
Ionization Detector (FID) for use in an organic carbon
detection system. Various configurations and arrangements
for each subsystem of the FID were investigated at the
outset. As anticipated, evidence gathered early in the
program fully supported the belief that the operation of
a sensitive FID unit on the Martian surface would require
fundamental design changes in detector elements currently
in use. The program accordingly evolved primarily into a
study of the basic operational and performance character-
istics of hydrogen flame ionization detectors. Theoretical
studies and analyses were correlated with laboratory experi-
ments in order to design and breadboard a pre-prototype
detector. Results of the study were twofold. First, it
achieved the unification of hydrogen flame ionization
detector technology. Second, it produced an improved
detector which ignites and sustains a flame at low pressures
and is generally superior to the best commercial detectors
available. Extension of this work should lead to a proto-
type flight detector suitable for various space missions.

I. INTRODUCTION

 This document contains the findings and conclusions
resulting from a research program conducted for the National
Aeronautics and Space Administration by Analog Technology
Corporation under NASA Contract NASW-1805, dated 17 September
1968. The program was directed toward the development of
a Pyrolysis/Hydrogen Flame Ionization Detector for use in
an organic carbon detection system on a MARS lander mission.

The purpose of preliminary life detection experiments
on the initial MARS lander will be to detect and analyze
life-derived organic matter in the soil. One of the most
compatible experiments for this purpose is one utilizing a
pyrolyzer/hydrogen flame ionization detector system. With
this system, a mechanically-processed soil sample is injected
into the pyrolyzer where it is heated in a closed atmosphere
to a specific temperature. Organic matter in the soil
sample is transformed to hydrocarbon vapor in an amount
proportional to its concentration in the sample. The hydro-
carbon vapor is transported to the hydrogen flame ionization
detector (FID) which yields a signal proportional to the total
number of hydrogen-carbon (C-H) bonds contained in the vapor
sample.

The pyrolyzer/hydrogen flame ionization detector
organic analyzer system is comprised of four functional
subsystems: the sample injection system; the gas-handling
and pneumatic system; the pyrolyzer; and the flame ionization
detector. Each subsystem was investigated, and various con-
figurations and arrangements were studied. However, the FID
itself determines most of the design constraints of this

and the other subsystems and, to a large extent, establishes
the overall performance characteristics of the analysis system.

Although preliminary studies were performed on the various
subsystems, it was determined early in the program that opera-
tion of the FID in essentially a vacuum environment would
require fundamental changes in existing detector designs.
Thus, the program evolved primarily into a study of the
operational and performance characteristics of hydrogen
flame ionization detectors.

Basically, the FID portion of the study consisted of
the following:

1. Literature survey and discussions with manufacturers
    of commercial FID's.

2. Detailed theoretical analysis of FID operating
    characteristics and mechanisms.

3. Correlation of the theoretical analysis with
    experimental results obtained from laboratory
    tests performed on several commercial detectors.

4. Extension of the theoretical analysis to the
    design of spaceworthy prototype detector.

5. Tests of the prototype detector.

6. Recommendations for further areas of investigation
    related to refinement of the detector into a
    completely spaceworthy FID.

The experimental study was conducted under two environments: standard conditions of temperature and pressure; and vacuum. Four commercial detectors were studied: Mino-Tek standard thermionic detector; Beckman GC-4; Perkin-Elmer 900; and Perkin-Elmer 226. Each of these detectors was characterized according to its respective current-voltage curves under the following parametric variations:

a) Voltage: 0-500 V

b) Hydrogen flow rate: 0-100 cc/min

c) Oxygen flow rate: 30-150 cc/min

d) Helium flow rate: 0-150 cc/min

e) Organic sample: methane in hydrogen at 0.2 and 5.0 mole percent.

f) Environmental pressure: 0-760 mm Hg

The pressure-ignition characteristics of the two Perkin-Elmer detectors, which provided the best basis for the evaluation of existing detectors, were as follows:

Perkin-Elmer 900

The ignition pressure limit was 250-300 torr with a 3-to-1 flow ratio of oxygen and hydrogen. Gas flow was reduced by a factor of 4 to achieve limit. Minimum hydrogen flow was 15 cc/min.

Ambient reduced pressure limit to sustain flame was
100 torr at a hydrogen flow rate of 15 cc/min. The flame
was ignited at 760 torr and ambient pressure was gradually
reduced. At 100 torr, the flame appeared diffused.

Perkin-Elmer 226

Ignition and flame reduced pressure limits were approxi-
mately 100 and 50 torr less than for the Perkin-Elmer 900,
respectively. The flame detached at approximately 100 torr
and was less severe with pure hydrogen. Detachment distance
appeared to be a function of jet-tip temperature. At 45 torr,
the flame was a blue haze surrounding the cathode. The
hydrogen flow rate at 25 torr was approximately 30 cc/min.
Larger flow rates undoubtedly due to the action of the detector
chamber flow restriction. At 2 torr, the electrode was relatively
hot due to catalytic combustion at the platinum surface.
Increases in pressure to approximately 75 torr reignited the
flame. With further increases, the flame reattached itself
to the jet tip.

The analytical and experimental results demonstrated
the magnitude of the problems at reduced pressure. Ignition
and flame combustion in vacuum are possible only in a pres-
surized FID unit combustion chamber. A special pre-prototype
detector for operation in a vacuum was therefore built to
demonstrate the feasibility of operation. The sensitivity
response of this detector at an environmental pressure of
1 atmosphere was 0.17 coulomb/g-atm C, which is superior
to that of most commercial detectors.

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The tests results at reduced pressures for the newly designed detector were:

(1) The detector sustained flames to environmental pressures of 3 torr.

(2) The detector ignited at all pressures and would sustain a flame below 200 torr with a cold detector.

(3) At detector temperatures higher than 170° C, reliable ignition was achieved and a flame was sustained at pressures to 3 torr.

II. THE HYDROGEN FLAME IONIZATION DETECTOR

A hydrogen FID is comprised of five functional elements:
the flame; the ignitor; the collecting electrodes; the detector
chamber; and the fuel and oxidant gases. The functional inter-
dependence of these elements dictates the operational and
performance characteristics of an FID unit. Thus, it became
essential during the study to develop a basic understanding
of the flame characteristics and their interaction with the
remaining FID elements. This task became more difficult as
the study progressed due to the absence of any unified treat-
ment and/or thinking on the subject in the scientific community.

FLAME

There are essentially two types of flames which can be
employed in this application, namely, premixed and diffusion
flames. In a premixed flame, the hydrogen and oxygen gases
are mixed in combustible proportions prior to burning at
the jet tip exit. The mixing process in a diffusion flame
is accomplished by a counter-diffusion mechanism of the
combustion reactants and products at a region in the flame
referred to as the reaction zone. Although each type of
flame has distinguishing characteristics, the study showed
that some characteristics are common to both flames. The
diffusion region of premixed flames is located in the region
surrounding the inner cone. The premixed region of diffusion
flames is located on the outer surface at the base of the
flame. Analytical and experimental investigations show that
these dual properties are very important to the stability
and combustion efficiency of the flames under reduced pressures.

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Premixed flames are primarily characterized by the propagation velocity of the flame-front. The flame-front propagation velocity of a hydrogen-oxygen flame is approximately 20 cm/s. A stationary flame at the jet tip is, therefore, maintained by matching the gas velocity to the flame-front propagation velocity. A negative or positive velocity imbalance will result in the flame striking down the jet tip or flame detachment, respectively. The flame-front propagation velocity is also important in establishing the location of the detector ignitor, which will be discussed later.

Premixed flames are decidedly more turbulent and the flame noise is correspondingly greater, i.e., there is a significant variation in the ion production rate with time. This behavior reduces the signal-to-noise ratio of the detector. The largest part of the noise arises in the inner cone of the flame, while that of the diffusion region is relatively small. It is essential that premixed flames be provided with an atmosphere that can support the diffusion flame combustion. Otherwise, premixed flames exhibit poor combustion efficiency which, in a pressurized chamber, will result in periodic explosions similar to those experienced with internal combustion engines.

Thus, the single advantage of a premixed flame cannot be exploited in this application because, at a minimum, two separate gas supplies and streams must be provided to furnish the detector with a useable flame. The pneumatic subsystem cannot be simplified over that of a detector utilizing a diffusion flame.

Diffusion flames are more difficult to characterize, because no single set of parameters peculiar to this type exists. However, diffusion flame combustion may be adequately described by considering the mass and energy transport processes supporting the reaction. Diffusion flames are stationary in the sense that there is nothing about them that is remotely analogous to a flame-front propagation velocity. The combustion reaction occurs on a closed surface near the surface of the flame. Since the concentrations of hydrogen and oxygen molecules at the reaction zone are zero, a hydrogen and oxygen diffusion potential is established. The radial distance of the reaction zone from the axis of the flame is determined by the difference in the diffusion coefficients and, to a lesser degree, by the thermal effects introduced by the heat capacity and thermal conductivity of hydrogen, water, oxygen, and diluent molecules. At the reaction zone, water vapor is also diffusing outward. It should be noted that the diffusion process described above results more from eddy diffusion than from a molecular diffusion process. The height of a diffusion flame is related to other parameters by the expression

$$h = \left[\frac{q\, X_{H2}}{2\pi K X_{sH2}} \right]^{1/2} \quad (1)$$

where   h = flame height

q = hydrogen volume flow rate

K = thermal diffusivity

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X_{sH2} = mole fractions of hydrogen in a stoichiometric mixture

X_{H2} = original mole fraction of hydrogen

The above equation is a simplification of the mass transport processes. However, the equation gives an indication of the effects of jet tip diameter and, to some extent, the introduction of helium as a fuel diluent. The mass and energy exchange at the reaction zone will be discussed in more detail in a later section.

Another important aspect of the diffusion flame is the premixed region at the base and its effects. The hydrogen-oxygen mixing is promoted by the negative pressure coefficient which is induced into the expanding hydrogen. Undoubtedly, there is local radial flow of oxygen at a rate exceeding the local rate of combustion. The properties of the flame at its base, therefore, are those of a premixed flame.

IGNITOR

The ignition of the FID flame is accomplished by adding energy to the combustible mixture at a sufficient rate to raise the temperature of the mixture to its kindling point (this ignition is accomplished only with a premixed flame). There are two fundamental types of flame ignitors which may be employed: a hot wire, and a spark ignitor. The two types differ only in the manner in which energy is introduced. Upon ignition of the

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combustible mixture, a flame-front with a propagation
velocity of approximately 20 cm/s radiates in all directions.
This flame-front is extinguished only when it reaches a
region where its composition is outside its flammability
limits. The flame can also be extinguished if it traverses
a region where energy is exchanged at a sufficiently high
rate from the flame-front to the surroundings so that a
drop in temperature below its burning temperature occurs.
(Examples of this phenomenon are the operation of flame
arrestors and safety lamps of the type used by miners.)
The relationship between the flame-front energy transfer
rate and extinction of the flame is characterized by a
parameter called the gas-quenching volume or diameter.
Several experimental arrangements can be employed to
measure the gas-quenching volume. The one most commonly
utilized is the flat-plate propagation volume where a
flame-front propagates through the cavity. The plates
are moved closer and closer together until it is impos-
sible to transport the flame through the cavity. The
perpendicular distance separating the two plates is the
quenching diameter of the flame. This means that the
electrode system surrounding or adjacent to the flame
must be designed to prevent quenching of the ignition flame.
Further study showed that a reliably-igniting detector will
operate at cross-purposes to an efficient ion collection
system. Thus, a flame completely enclosed by an ion collecting
surface will quench the ignition flame-front when its effective
separation is less than the quenching diameter of the gas
mixture.

The quenching diameter is the function of gas total
pressure which was found to be inversely proportional to

the cube of absolute pressure. A detector operating at a
total pressure of 1/2 atmosphere will require a minimum
electrode spacing eight times larger than that of a detector
operating at 1 atmosphere. It is obvious that there will
be separation limits placed on the electrode system other
than those imposed by thermionic emission. It is possible
that only a minor reduction in flame noise can be accomplished
by shrouding the flame because of the ignition reliability
problems. Some of these problems may be alleviated by
operating at a higher pressure which will induce larger
and more severe free-convection currents as will be discussed
later.

The most reliable ignition element which may be employed
in this application is a hot wire surface. It is superior
to a spark ignition system, because the associated equipment
and elements required to produce the high temperature surface
are simpler than those of a sparking system. Also, recharging
and discharging of condensers will not be required. An added
reliability factor can be included with a hot wire ignitor
by fabricating the hot wire of a material which will promote
catalytic combustion. The most likely catalytic materials
are platinum and palladium. In the event that the ignitor
heating system fails, the heat of reaction produced by the
catalytic combustion of hydrogen and oxygen on the catalytic
surface is sufficient to raise its temperature to that required
to ignite the gas mixture.

Aside from the quenching problem, it was experimentally
demonstrated that the location of the ignitor surface may be
important in the design when not maintained within given limits.

The velocity of the combustible gas mixture at any point between the ignitor surface and the detector jet tip must never exceed the propagation velocity of the flame-front. In fact, the velocity should be much less in order to assure reliable ignition. The flame-front velocity is approximately equal to the velocity of the gas at the jet tip. Deviations from this equilibrium condition will allow the flame to strike back down the detector jet tip or the flame will detach itself and stabilize at some position above the jet. The equilibrium position is determined by the exchange of the gas from the jet tip. As the gas expands, the velocity is reduced to the point where it is equal to the flame-front propagation velocity. This discussion applies only to diffusion flames because of the premixed nature of a diffusion flame.

The location of the ignitor surface is also important from the standpoint of ignition explosion. It can be seen that, as the ignitor surface is moved away from the main gas stream, a more or less homogeneous mixing of hydrogen and oxygen will occur throughout the volume of the chamber. Thus, a large pressurized chamber with the ignitor at a relatively large radial distance from the jet tip could easily ignite with a violent explosion. It is not desirable to permit ignition in this fashion, unless the chamber length-to-diameter ratio is within specific limits.

The temperature of the ignitor wire is ordinarily maintained at several hundred degrees above the ignition temperature of the gas. The wire temperature is established by the heat transport properties of the gas mixture, the surface area of the wire, and the velocity of the gas. More accurately, the temperature of the ignitor is related to Nusselt, Prandtl,

and Reynolds numbers. The gas velocity, density, and other properties can be related to the geometry of the ignitor and the final burning temperature as

$$T_b = \frac{\frac{E}{2R}}{\ln \left[(B/A)^2 \frac{D}{W} \gamma \right]} \qquad (2)$$

where T_b = final burning temperature

    E = activation energy of the chemical reaction

    R = gas constant

    γ = kinematic viscosity

    D = diameter of the wire

    W = rate of reaction (burning)

  $B \ \& \ A$ = constants related to the reaction order ($B=1/2$, $A=1$ for $H_2 = 1/2$ $O_2 = H_2O$

Equation (2) is utilized in the heat balance relationship at the ignitor surface relating the dimensionless moduli cited above.

$$q = \frac{A\mu}{D} (Pr)^u (Re)^m (T_i - T_k) \qquad (3)$$

where q = ignitor power

$$A \quad = \quad \text{ignitor surface area}$$

$$\mu \quad = \quad \text{gas mixture viscosity}$$

$$T_i \quad = \quad \text{ignitor surface temperature}$$

$$T_k \quad = \quad \text{burning temperaute}$$

$$Pr \quad = \quad \text{gas mixture Prandtl number}$$

$$Re \quad = \quad \text{gas mixture Reynolds number}$$

$$u \,\&\, m \quad = \quad \text{constants depending upon temperature and Reynolds number range}$$

Equation (3) is used to compute the ignitor power requirements. The local Reynolds number adjacent to the ignitor surface should be used in this noted equation.

COLLECTING ELECTRODES

The design of the collecting electrodes must incorporate features which provide maximum sensitivity and, at the same time, promote aerodynamic conditions to prevent the internal circulation currents in a pressurized combustion chamber from disturbing the flame. Also, the electrode spacing or diameter in the core of a cylindical electrode must be greater than the quenching diameter of the gas mixture (≈ 0.1 @ 1 atm).

The electrode efficiency and collecting characteristics can be assessed by utilizing the sensitivity parameters

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and the I-V properties. The sensitivity is the measure of
the total number of coulombs collected by the electrode for
every g-atm of carbon through the flame, i.e., coulombs/g-atm.
At atmospheric pressure, utilizing optimum flow rates of
hydrogen, helium and oxygen, the sensitivity parameter is
near 0.2 - 0.5. The shape of the detector current-voltage
curves in the plateau region and/or the voltage of the knee
can also be employed to establish the degree of competitive
collection, thermionic emission, ion blow-by and, in some
cases, the detrimental influences of the space charge. An
I-V curve with a positive linear slope in the plateau region
is characteristic of thermionic emission. An I-V curve with
a negative slope in the plateau region is characteristic
of competitive collection. An I-V curve without a knee
or plateau but with a positive low-level slope ordinarily
indicates ion blow-by. All the detectors investigated were
characterized in this manner.

In order to establish the electrode system's theoretical
performance limits and the relative importance of its para-
meters, an investigation of the electrode process was conducted.
The results of the study will be exceedingly valuable in the
design of the electrode system for the flight prototype detector.

Ion blow-by and space charge effects may establish the
electrode geometry and, perhaps the oxygen flow rates. It
is anticipated that the ion collector may approximate a hollow,
small-diameter (D = 0.1 cm) cylinder which completely surrounds
the flame over its entire length. The jet tip could be the
electron collector. The oxygen will flow through the cylinder
and prevent or minimize the effects of circulation within
the chamber. Care must be exercised to maintain a favorable
oxygen flow condition (Re < 100).

It was analytically determined that the space-charge
problem which can assert itself is chiefly concerned with
the electrode geometry. Since the flame is a relatively
good conductor, the electric field in it is zero and the
small voltage drop is due only to ohmic drop. Therefore,
the ion currents are diffusion-limited and can be expressed
by:

$$I = SN_+ \, e\sqrt{\frac{KT_+}{2\pi M}} \qquad (4)$$

where

I = ion current

S = area of the electrode surface
sheath established by the space
charge

N_+ = average ion concentration in the
flame

e = electronic charge

K = Boltzmans constant

T_+ = ion temperature as defined by
Langmuir probe experiments

M = ion mass

In cases where the inside surface of small-diameter
cylindrical electrodes are employed, it was observed that
the diffusion-limited current as defined by equation (4)
is a decreasing function of electrode voltage. This
behavior is primarily due to the increase in the electrode

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sheath thickness with voltage. Thus, when utilizing the inside surface of a cylinder, the diffusion area (S) is reduced by a corresponding amount.

THE DETECTOR CHAMBER

The primary design considerations of the detector chamber were those associated with its temperature, water condensation, and aerodynamic properties.

The chamber design incorporated features which provided a minimum disturbance to the flame and permitted the detector chamber to reach temperatures near 110^{0} C as rapidly as possible in order to prevent water condensation in the pressurized unit. Specially-located dead-volume chambers and/or circulation baffling systems may also have to be provided to dampen the circulation currents.

III. DETECTOR SENSITIVITY AND FLAME NOISE

The detector sensitivity and flame noise are related
to the ionization process in the flame. The detector
sensitivity can certainly be increased by factors nearing
100 by altering the ionization kinetic parameters. The
noise of flames burning in a pressurized chamber is of
large amplitude and relatively low frequency (2 - 3 Hz).
It is also believed that the flame noise can be attenuated
to some degree by controlling the kinetic parameters of
the flame.

IONIZATION MECHANISM

The process by which ions are formed in flames has
been in dispute for several years. However, it has been
quantitatively described as a chemi-ionization process.
Several theories based on specialized energy exchange
processes due to thermal energy transfer could not be
used to prove that sufficient energy is available to
produce the number of ions which had been measured in
flames. Other theories related to impurities arising
from carbon particles, sodium, potassium, and other
elements have also met with failure in this respect, that
is, the number of ions produced does not nearly match the
concentration level measured by experiments.

The chemi-ionization process explains both the
qualitative and quantitative aspects of the mechanism.

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It is believed that sufficient energy is imparted to
a given number of hydrocarbon molecules existing in
the complex activated state to induce a transition to
the ionized state of approximately 13.29 eV. The
concentration level of hydrocarbon ions predicted by
this method is approximately that found by experimental
means, which is 1×10^{10} ions per cc. These considerations
show that only a very small fraction of the total number
of hydrocarbon molecules available is ionized. The mole
fraction is approximately 10^{-6}. This discussion indicates
that a hydrogen flame ionization detector can be made more
sensitive to the detection of hydrocarbon molecules only
by increasing the fraction of ionized hydrocarbon molecules.
In many respects, some apparent sensitivity can be realized
by increasing the fuel flow rate to the detector. This
technique, however, is usually misleading for continuous
measurements, primarily because the amount of sample
increases with the hydrogen flow rate. In special
applications where a pyrolyzed sample of hydrocarbon
is injected into the hydrogen stream, the total number
of coulombs produced is proportional to: the total number
of hydrocarbon molecules ionized; the concentration of
hydrocarbom molecules that have been pyrolyzed; and a
combination of these two things. The total number of
hydrocarbon molecules ionized from a given sample is
proportional to the structure and temperature of the

flame. Since a diffusion flame is best suited for flame
ionization detectors, the structure of the flame may
be characterized by the total area of the flame reaction
zone. Some errors are introduced in applying this rule
because a vertical concentration gradient of ions
which is a function of the flame height, exists in
the reaction zone.

At a reduced pressure of about 0.5 atmosphere, the
ion concentration for the steady-state condition may
change by a factor of 3, with the greater concentration
of ions existing near the jet tip. Several means by
which the flame structure can be altered to produce a
larger reaction zone surface area are available. The
most common technique employed for commercial applications
is the use of helium gas as a fuel diluent. Detector
sensitivity has been increased by an order of magnitude
by diluting the hydrogen with approximately one-third
helium. The sensitivity of the detector was increased
from 0.02 coulomb/g-atm C to 0.2 coulomb/g-atm C.

Again, this increase in sensitivity is accomplished by
altering the structure of the flame reaction zone. Not
only is the area of the reaction zone increased but there
is sound evidence that the reaction zone becomes more
diffuse or thicker with the amount of helium in the
fuel. The sensitivity ordinarily increases with the

addition of the helium until a peak sensitivity is reached; beyond this, the further addition of helium causes a decrease in sensitivity. Sensitivity decreases are caused primarily by a reduction in temperature of the reaction zone due to its having a higher thermal conductivity than that of water vapor and oxygen.

The transport properties of hydrogen and helium are relatively similar when compared to oxygen, nitrogen, carbon dioxide and water vapor. Therefore, it is apparent that the primary changes introduced by helium are effective only in the product side of the reaction zone. Aside from the fact that an additional amount of inert mass must be heated to the reaction temperature by the heat of combustion, the thermal diffusivity and the diffusion coefficient on the product side are greatly altered. Hydrogen, helium and the ordinarily small amount of hydrocarbons and some impurities diffuse from the core of the flame into the reaction zone. On the product side, water vapor, CO_2, unburned hydrocarbons and intermediate products diffuse away from the reaction zone and the oxygen diffuses toward the reaction zone. Helium, when present in the hydrogen stream, also diffuses away from the reaction zone on the product side. The presence of helium very definitely alters the properties of the system on that side of the reaction zone. The thermal conductivity of helium is

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approximately 10 times greater than that of the other gases present and its diffusion coefficient is approximately 5 times greater. Its heat capacity is also 5 times greater.

A quantitative description of the kinetic changes introduced by helium can be described by considering the mass and energy transport mechanisms in the system. Most of the changes occur on the product side of the reaction zone. However, the increase in the total surface area of the reaction zone is induced by the difference in the diffusion coefficient of helium and hydrogen in water vapor as opposed to the diffusion coefficient of water vapor in hydrogen. Also, it is apparent from dilution considerations alone that a larger area with a greater transport distance will be required to attain a stoichiometric mixture with hydrogen and oxygen. This transport distance is a logarithmic function of the flame reaction zone radius, the diffusion coefficient of helium in hydrogen, and temperature. The sensitivity is also increased by a factor proportional to the increase in the height of the flame. The increases in sensitivity due to the flame height are also reflected in the increases in reaction zone area and are approximately equal to the radial increases.

Further analytical investigation was conducted to establish the feasibility of increasing the detector sensitivity by increasing the flame reaction zone area, such as with a flat flame possessing a large aspect ratio. Calculations demonstrated this feasibility, as well as revealing the fact that this approach offers distinct advantages in the ion-collection efficiency of

the electrodes. However, for the relatively low-volume
flow rates in an FID, there is no aerodynamic difference
between conical and flat flames for aspect ratios of 20
and below. It was concluded that aspect ratios greater
than 100 were required to fully exploit the advantages
of a flat-flame. The approximate dimensions of a flame
holder for this aspect ratio would be 0.635 cm by 0.0635 mm.
A flat flame holder utilizing these dimensions was fabricated
and tested. The volume flow rates and Reynolds number were
equivalent to those of the jet tip in the GC-4 detector.
It showed a sensitivity parameter of one-half that of the
conical. However, it was later established that approxi-
mately 90% of the sample was lost through leaks. Attempts
to seal the flat-flame holder failed. The test results,
nevertheless, were very encouraging.

FLAME NOISE

There are ordinarily two mechanisms which contribute
to the detector signal-to-noise ratio. Associated with the
normal pyrolyzed sample is a blank noise reading which is
as yet not satisfactorily explained. The signal current
normally associated with the blank reading is approximately
10^{-12} A. This level varies considerably with the thermal
history of the pyrolyzer-sample injector system, the
cleaning procedures employed, and, in some instances,
the particular geographic region of operation. The blank
background current level must be quantitatively explained
in order to promote more accurate sample determinations.
Several theories attempting to explain the properties
and sources of the blank have recently been proposed.

The theory gaining most popular favor is that associated with a contamination process which arises from adsorbed molecules on the surface of the kinetic elements of the system. Regardless of the source, the nature of the impurities remain unexplained. For example, hydrocarbon impurities would seriously limit the sensitivity of the detector, because procedures implemented to increase the current level will also increase the signal-to-noise ratio of the detector, that is, amplification of the current level would also promote amplification of the blank background level. A simple test can be devised to identify the hydrocarbon origins of the impurities. If, indeed, the impurities are hydrocarbons, then it is probable that only a small fraction of the total number are ionized in the flame. Thus, the addition of helium to the fuel hydrocarbon mixture would certainly ionize a greater fraction in the flame. To relate the background blank current level to the helium flow rate into the detector would be a simple matter.

Another proposal suggests that the blank current level may be due to potassium and sodium impurities. The fraction of potassium and sodium molecules ionized in the hydrogen flame is almost complete. Thus, additions of helium and any other means which may be employed to increase the flame reaction zone surface area would not produce an increase in the blank background current level.

Another anomalous characteristic of the blank reading is its lack of consistency. Contamination by hydrocarbons in the preceding samples would probably not produce these variations. The adsorbing and deadsorbing properties of

of the construction materials used in the pneumatic and
sample-handling systems of the FID unit are primarily
well established and their characteristics well-known.

A more serious source of flame noise arises from the
aerodynamic disturbances in the FID chamber as mentioned
earlier. A hydrogen flame is usually operated in the
laminar flow region well below a Reynolds number of 2200.
The commercial hydrogen flame detectors investigated in
this study all operated below 320. Thus, flame noise
due to disturbances between the flame and the supporting
atmosphere is minimized. The aerodynamic noise is that
induced by gas circulation currents in the detection
chamber which become more severe as the pressurized
chamber vent is reduced in size. For a pressurized detec-
tor such as that operating in a vacuum, the equilibrium
vent diameter is approximately 0.010 inches, and erratic
unpredictable aerodynamic disturbances ensue. The flame
noise arises from the interaction of the flame with the
recirculating gas. Changes in the flame reaction zone
surface area are induced. Under ordinary near-steady-
state conditions, a low-frequency, large-amplitude noise
has been observed in the pressurized detector. It is
important that the detector chamber include baffling sur-
faces and recirculation subchambers. This arrangement
can plausibly be promoted by locating the flame in a
relatively high velocity region of the oxygen. It will
minimize the effect of the free-convection currents which
constitute the driving mechanism of the circulation.

Determination of the flame noise level, after the
aerodynamic disturbances have been minimized, will establish

the maximum signal-to-noise ratio of the detector.
Obviously, if the signal-to-noise ratio of a detector,
considering only the aerodynamic flame noises, is smaller
than the signal-to-noise ratio of the detector established
by the blank current level, a study of the characteristics
of the blank noise would be superfluous. However, if the
converse is true, we should then study the possibility
of establishing the characteristics and sources of the
blank in order to reduce it to a level comparable to the
signal-to-noise ratio of aerodynamic flame noise.

IV. OPERATION AT REDUCED PRESSURES

The FID performance is established by the atmospheric pressure constraint. The functional dependence is fundamentally ascribed to pneumatic conditions defined by the hydrogen-helium, oxygen, and atmospheric pressures. Operation of an FID unit designed for relatively high atmospheric pressure specifications, e.g., 760 torr, is not possible below certain reduced pressures without major changes to the flame chamber and/or implementation of gas flow and pressure controls.

A typical situation arising with commercial FID units is that which develops as the atmospheric pressure is reduced. As the H_2-He to atmospheric pressure ratio exceeds the critical pressure ratio, the linear velocity of the gas at the jet exit is equal to the acoustic velocity. Gas flow conditions at Mach one evidently do not permit the operation of an FID unit. The gas velocity at the jet exit will be approximately 200,000 cm/s and the Reynolds number, 31,200. These are clearly turbulent flow conditions. The Reynolds number should be below 2,000 and is usually maintained below 100. Thus, the Reynolds number must be reduced by a minimum factor of 200. Assuming the flame can be ignited and that the gas at the jet exit is at 1,000° C, the Reynolds number will be reduced by a factor of 2.5 to 12,500 by gas viscosity increases. The diameter of the jet exit may be reduced but only by also reducing the flame diameter. The most effective way to reduce the Reynolds number is apparently by reducing the gas flow rate and delivery pressure.

For operation at an atmospheric pressure of 5 millibars, the delivery pressure must not exceed 10 millibars to prevent

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a choked condition at the jet exit and 6 millibars to produce favorable gas flow and pressure conditions. A relatively low gas flow rate will result. Thus, a small flame with a correspondingly small signal will be produced. A flat flame can be employed to advantage in this application to increase the signal and stabilize the flame. Other problems exist in igniting the FID. Aerodynamic, chemical, and heat-transfer effects affect the ignition characteristics at reduced pressure to compound the problem. As reported earlier, a combustible mixture or only a premixed flame can be ignited. Thus, the gas velocity at the ignitor surface or the region adjacent to the reaction zone of the diffusion flame must never exceed the flame-front propagation velocity of the premixed flame. The flame propagation velocity has been estimated never to exceed 20 cm/s. Therefore, the velocity profile of the expanding gas jet must be controlled to a degree where ignition of the diffusion flame can be achieved. Thus, the flame will detach itself from the jet tip due to excessive gas-jet velocity. Also, a relatively large degree of fuel and oxidant mixing will occur in the transition region where the gas velocity decreases. The ion concentration gradients normally experienced with diffusion flames will be distorted. The degree of flame detachment will prohibit using the jet tip as the positive electrode because of the relatively large distance the electrons will be required to traverse despite their large mobility. All these processes determine the critical location of the ignitor within the FID chamber.

The 5-millibar reduced pressure condition appears to have excluded the possibility of igniting the commercial detectors at our disposal. Calculations also indicated the FID would be outside the flammability limits for ignition.

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The gas velocity appears to be greater than the flame-front propagation velocity in the region of the ignitors. The ignitors of the detector had to be altered to permi changes of their effective location. Higher ignit-r surface temperatures were required to supply sufficient power for ignition. An increase in che ignitor surface area would have helped for identical reasons. It is also possible that the flame will extinguish itself if the direction of flame propagation is not correct. This condition arises when the relative position of the ignitor and reaction zone of the diffusion flame permits flame propagation in the direction of a lean combustible mixture only. This possibility is enormously increased with detached flames possessing relatively large premixed regions.

Some of the problems in reduced-pressure operation were alleviated by restricting the gas flow from the combustion chamber to the atmosphere. The FID would operate at higher gas pressures and gas flow rates. It was analytically determined that other problems, however, are introduced with this design. At 5-millibars pressure, the boiling point of water is 1° C. Pressurization of the chamber increases the boiling point, e.g., at 50 millibars, the boiling point is 39° C. The temperature of the chamber walls and all components must be maintained above the water boiling point to prevent condensation. These problems were experienced with one of the commercial detectors whose flow from the chamber is restricted to only a small degree. The amount of restriction required for this application will probably be much greater. It is likely that the chamber can be heated above the boiling point and maintained at a given temperature with only heat of combustion. Nevertheless, the commercial

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detectors studied were equipped with heating elements and temperature indicators and controls for the warmup phase.

Another problem associated with flow restriction of the chamber is that of reaching chemical equilibrium of the combustion products in the chamber within a reasonable time. The partial pressure of water vapor will constantly change until equilibrium is attained. During this time, flame temperatures drop and the FID response changes continually. It is not certain to what extent this condition will affect the signal in time.

V. TEST RESULTS OF IGNITION AND COMBUSTION AT REDUCED PRESSURES

Experimental investigation of commercial FID operation at reduced pressures demonstrated that combustion, ignition, ion distribution, and structural characteristics of flames are considerably altered by operation at reduced pressures. Also, the pneumatic conditions arising at reduced pressures promoted turbulent noisy flames. At sufficiently reduced pressures, it is not possible to initiate flame ignition and sustain flame combustion. Analytical and experimental investigations show that approximate ignition and combustion-reduced pressure limits are 200 and 100 torr, respectively.

TEST APPARATUS

The test equipment and configuration required to obtain maximum information from test results is of great importance. Therefore, the equipment used to support this study is described according to the major classifications of test functions.

Gases

Matheson high-grade chromatography gases were utilized to insure accuracy. Ultra-pure oxygen, hydrogen and helium were used to perform precise blank current measurements. Hydrogen diluted with 5% or 2/10% methane was used to measure detector efficiencies with simulated steady-state samples.

Filters

Chemical Research Corporation Dririte-desiccant filters were placed in all gas lines to assure minimal

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contamination due to handling. These filters were specifically designed to remove moisture and oil.

Valves

Matheson high-grade chromatography metering valves and Hoke chromatography toggle valves proved to be excellent for highly sensitive control of gas systems.

Regulators

Matheson high-grade chromatography regulators provided accurate control of delivery pressure for all gas lines.

Flow Meters

Matheson predictability flow meters were used in conjunction with adjustment curves compensating for the type of gas, temperature, and pressure.

Pressure Monitors

Two types of pressure detection systems were applied. A Cenco mercury manometer was used to monitor pressures with absolute values less than one atmosphere. Sensitive Consolidated Electro-Dynamics potentiometric pressure transducers were used to monitor pressures with absolute values from one to three atmospheres.

Vacuum System

The vacuum system consisted of a Cenco Hy-Vac mechanical and diffusion pump. Ajean Vac-Tronics feedthroughs and seals aided in obtaining a well-defined subatmospheric environment.

Plumbing

Swagelok, Tylok and Gyrolok gas fittings and tubing were used in all plumbing applications.

Electrometer

An ATC-designed and -tested electrometer monitored detector currents. This solid-state electrometer was chosen because of its high input impedance, low noise, fast response and mechanical range switching capabilities.

Thermocouple System

Ice-bath-referenced, iron-constantan thermocouples with a potentiometric readout were used for temperature monitoring.

Power Supplies

In general, it was possible to use standard laboratory supplies. Two special applications required a 6-V high-current supply and a Power Design 5005 precision millivolt source. The 6-V supply was used for the hot wire ignitor and consisted of a Variac and a 6-V filament transformer.

Detectors

Beckman GC-4, Perkin Elmer 900, Perkin Elmer 226, and Mino-Tek standard detectors were used.
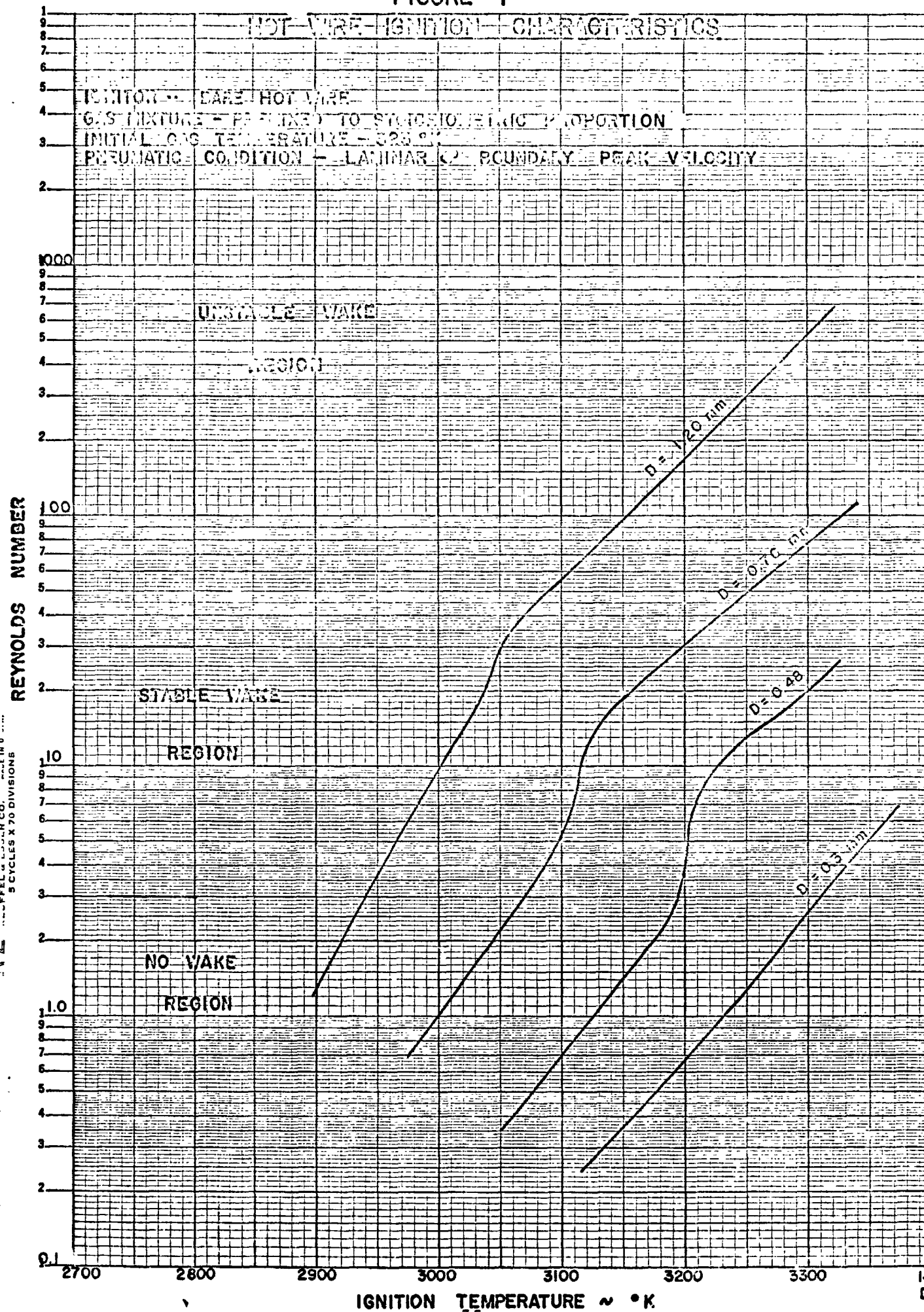
IGNITION AT REDUCED PRESSURES

Ignition of a diffusion flame is accomplished by heating a given minimum volume of gas in one of its premixed

regions to its ignition temperature. The premixed regions include the area at the base of the flame near the rim of the jet tip or an area downstream where sufficient hydrogen and oxygen mixing has occurred by a diffusion process.

Ignition failure may result because the supply of ignition power to the premixed quenching volume is insufficient (the combustible mixture at the ignitor being outside the compositional flammability limits), and because the gas velocity exceeds the flame-front propagation velocity at any point between the ignitor surface and the reaction zone of the flame.

The minimum power requirements for ignition are related to the ignition surface temperature and its exposed surface area. Figure 1 illustrates the relationship of these parameters to the premixed gas Reynolds number at the ignitor. As Reynolds number is increased, the surface temperature of a hot wire ignitor must be correspondingly increased to provide sufficient ignition power to the quenching volume. Higher temperatures are required to transmit the power because the contact time of a gas particle with the hot surface is reduced as Reynolds number is increased. Figure 1 also illustrates the importance of the pneumatic conditions and position of the ignitor within the FID chamber. It must be located in a region where the Reynolds number of the combustible mixture never exceeds the limit defined by the wire diameter. Also, a combustible mixture must surround it and a combustible mixture path between the ignitor and the jet tip must exist. An important aspect, not directly shown in Figure 1, is that the gas velocity must never exceed the flame-front propagation velocity.

FIGURE 1

HOT WIRE IGNITION CHARACTERISTICS

IGNITOR – BARE HOT WIRE
GAS MIXTURE – PREMIXED TO STOICHIOMETRIC PROPORTION
INITIAL GAS TEMPERATURE – 328 °K
PNEUMATIC CONDITION – LAMINAR 2) BOUNDARY PEAK VELOCITY

UNSTABLE WAKE

REGION

D = 1.20 mm

D = 0.70 mm

D = 0.48

STABLE WAKE

REGION

D = 0.3 mm

NO WAKE

REGION

REYNOLDS NUMBER

IGNITION TEMPERATURE ~ °K

35

1-22-69
DPL/83

At reduced pressures, the converse is quite likely true when the gas flow rates, hydrogen Reynolds number at the jet tip, and Mach number at the jet tip are not inter-related in a specified manner and maintained within pre-scribed limits. The conditions become unsatisfactory at the point where the chamber pressure is low enough to promote turbulence in the expanding gases.

Figures 2 and 3 illustrate the preliminary results of tests to establish the ignition characteristics of a commercial detector for which a relatively short reaction zone is obtained. In this case, the flame is quenched in the premixed region by the metallic jet. A nonmetallic jet tip will, of course, extend the lower flow rate limit because it does not possess any major conductive heat transfer properties.

Another important aspect of flame combustion character-istics not shown in Figure 3 is the detachment of the flame from the jet tip. At high chamber pressures, the flame exhibits the normal conical shape with an approximate height of 0.125 inches. As chamber pressure and hydrogen flow rate are reduced, the flame height is shortened cor-respondingly. At a chamber pressure of approximately 300 torr, the flame detaches itself from the jet tip. Further reductions in chamber pressure and hydrogen flow rate diminish the flame height still further and the detachment distance is increased. At chamber pressures near 100 torr, the flame height and the detachment dis-tance are both approximately 0.06 inches. The flame diameter was approximately that of the jet tip, 0.025 inches, and thus assumes a more hemispherical than conical shape.

FIGURE 2

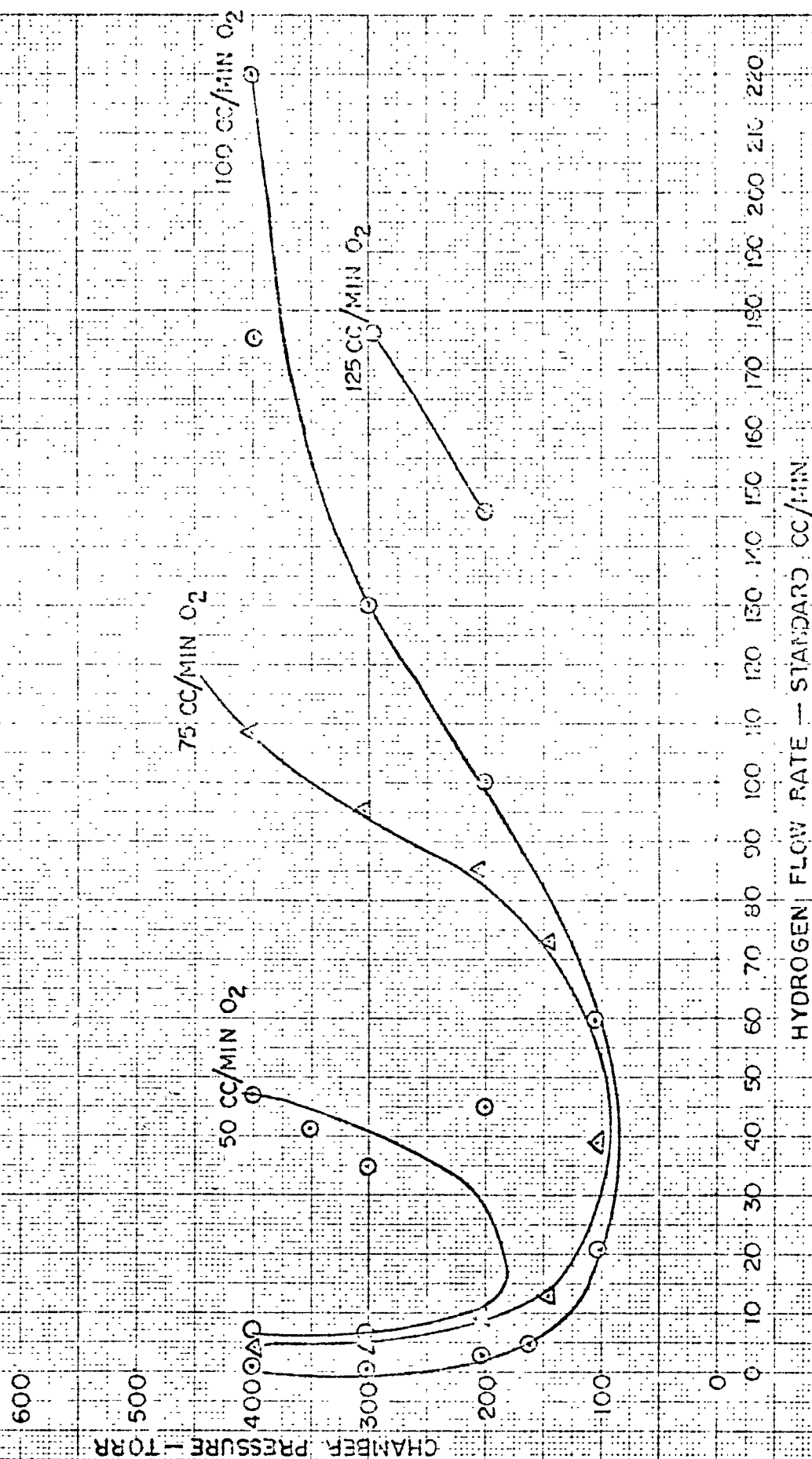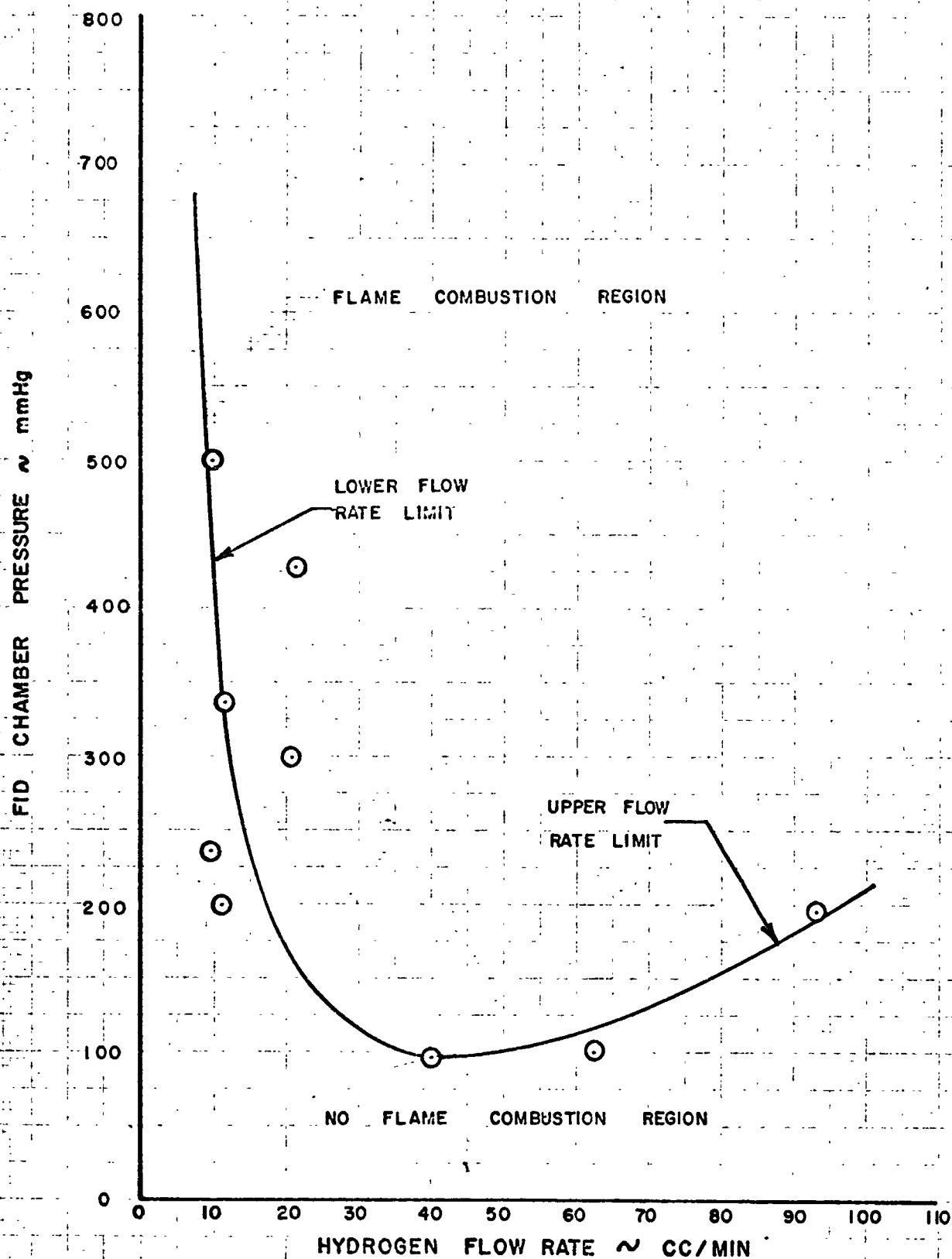HYDROGEN FLAME IONIZATION DETECTOR IGNITION CHARACTERISTICS

FID-PERKIN/ELMER 226

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FIGURE 3

FID FLAME COMBUSTION CHARACTERISTICS

OXYGEN/HYDROGEN FLOW RATE RATIO – 4:1

FLAME COMBUSTION REGION

LOWER FLOW RATE LIMIT

UPPER FLOW RATE LIMIT

NO FLAME COMBUSTION REGION

FID CHAMBER PRESSURE ∼ mmHg

HYDROGEN FLOW RATE ∼ CC/MIN

I-22-69
DPL/es

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FID OPERATION WITH PRESSURIZED COMBUSTION CHAMBER

The ignition and flame combustion pressure character-
istics of FID units establish to a large degree the design
constraints of the chamber. Figures 2 and 3 establish the
lower pressure limit at 190 and 100 torr for ignition and
flame combustion, respectively. Therefore, the chamber
pressure and vent port characteristics are constrained to
these performance limits. It may be desirable to operate
the FID at higher chamber pressures in order to attain larger
flames with correspondingly larger signals and the capacity
to ionize more of the hydrocarbon sample.

Pressurization of the FID chamber is accomplished by
increasing the total gas flow rate in the chamber and/or
by incorporating a restrictor at the chamber exit. Figure 4
graphically illustrates the relationship between the length,
diameter, flow rate, and pressure drop of a capillary
restrictor. Since weight, space, and ease of operation are
prime factors in the design of the FID unit, a restrictor
diameter below 0.015 inches will be required to maintain its
length to a few inches. Two restrictors, comprised of 0.010
and 0.006-inch tubes were fabricated and assembled. Tests
were then conducted to assess the detector. The detector
failed to ignite completely below chamber pressures of
150 mm Hg. Other ignition failure limits were established
at lower and upper hydrogen gas flow rates. The upper limit
was established by a gas velocity which exceeded the flame-
front velocity. The temperature of the ignitor surface may
also have been too low to supply sufficient power to the gas.
The lower limit in the lower chamber pressure regions also

failed to ignite for the identical reasons. At higher
chamber pressures, ignition failure was primarily due to
the unavailability of combustible mixtures inside the
compositional flammability limits.

The shape and limits of the ignition region can
be significantly changed by relocating the ignitor. Thus,
dependency on the chamber pressure, the location of the
ignitor and its relationship to the gas velocity profile
within the chamber are important design considerations.

FLAME COMBUSTION CHARACTERISTI. T REDUCED PRESSURES

The size and shape of the flame are established by
the hydrogen flow rate, chamber pressure, and the flame
holder shape. Figure 3 illustrates the preliminary results
of tests to establish some of the flame combustion charac-
teristics of a commercial detector employing a circular
jet tip. A flame cannot be sustained at chamber pressures
below 100 mm Hg. As chamber pressure is increased, larger
hydrogen flow rates are required to sustain a flame.

The upper flow rate limit is established by the maxi-
mum hydrogen gas velocity prior to exceeding the flame-
front velocity. As the hydrogen flow rate is increased,
the gas velocity increases and eventually, the flame is
blown away. This condition arises from the nature and
structure of diffusion flames which possess a premixed
flame structure at the base of the flame adjacent to
the rim of the jet tip. Consequently, this region will
exhibit a flame-front velocity which propagates in a
direction opposite to that of the jet gas velocity. In

the lower FID chamber pressure region of the lower flow
rate limit, the flame is blown away for identical reasons.
However, at the higher FID pressures of the lower flow
rate limit, the flame is severely reduced in height to
ignition and flame combustion characteristics of the
FID chamber.

Fundamental problems were introduced to the detector
when it w ' operated with a pressurized unit. It is cer-
tain that ₋ne equilibrium partial pressure of oxygen,
helium and water vapor in the chamber will be proportional
to the respective gas flow rates. Thus, operation at
gas flow rates suitable for an open detector will yield
water vapor mole fraction between 0.30 and 0.35. This
gas composition is not conducive to sustaining a stable
flame. According to mass action considerations, the flame
conbustion process rate should be diminished.

The FID vent port characteristics are illustrated
by Figure 4. Operation at chamber pressures above 25 mb
will result in a pressure ratio at the port exit above
the critical valve and, therefore, an exhaust gas Mach
Number of 1. The vent port line length required to achieve
the required flow restriction and pressure drop is given
by the equation below:
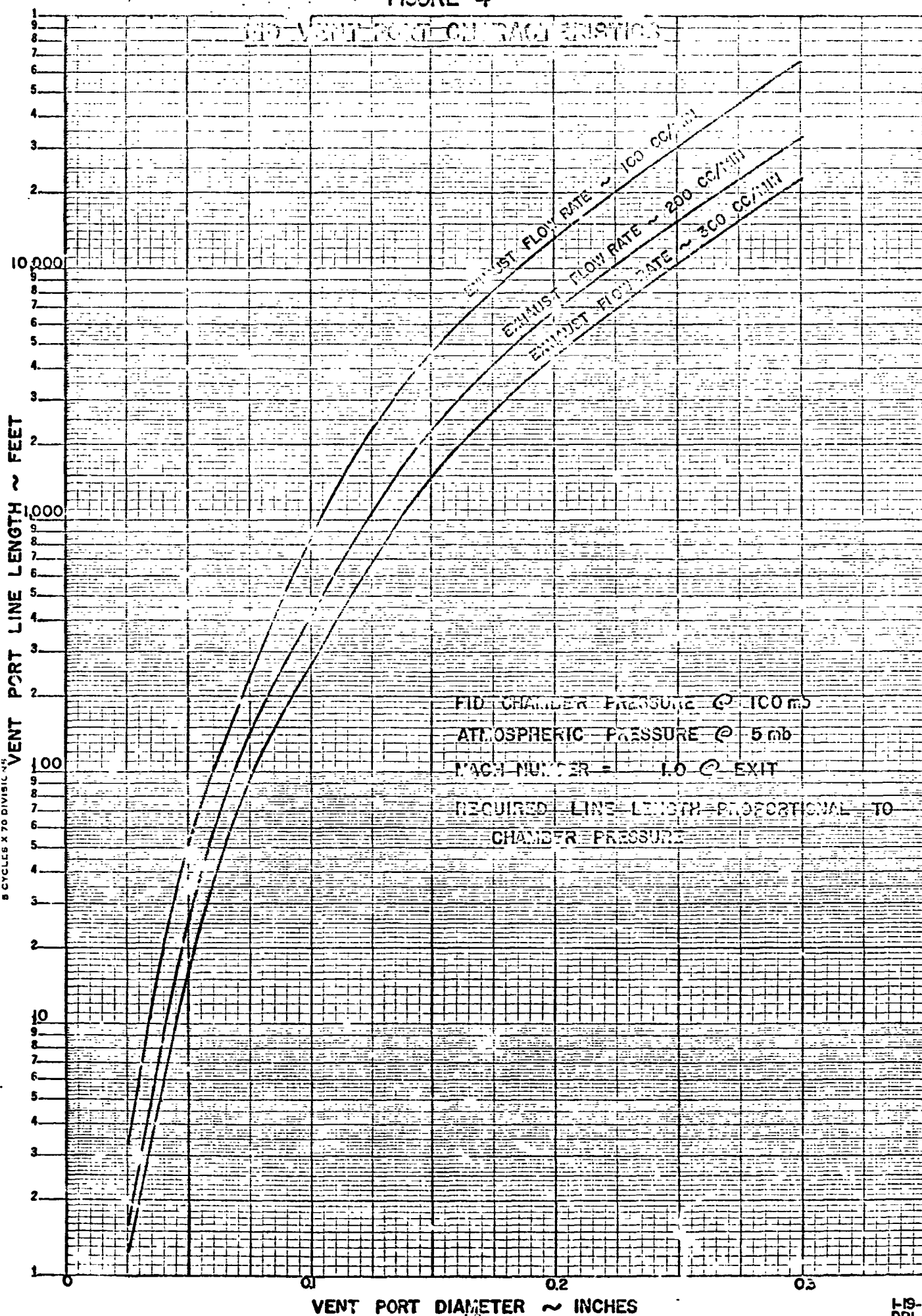
$$L = \Delta P \quad 39.6 \gamma D^5 / f(w)^2,$$

$$L = \text{vent line length, FT,}$$

$$\gamma = \text{exhaust gas density, lb/FT}^3$$

$$f = \text{gas friction factor, dimensionless,}$$

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FIGURE 4

FID VENT PORT CHARACTERISTICS

Curves labeled:
- EXHAUST FLOW RATE ~ 100 CC/MIN
- EXHAUST FLOW RATE ~ 200 CC/MIN
- EXHAUST FLOW RATE ~ 300 CC/MIN

FID CHAMBER PRESSURE @ 100 mb
ATMOSPHERIC PRESSURE @ 5 mb
MACH NUMBER = 1.0 @ EXIT
REQUIRED LINE LENGTH PROPORTIONAL TO
CHAMBER PRESSURE

Y-axis: VENT PORT LINE LENGTH ~ FEET

X-axis: VENT PORT DIAMETER ~ INCHES

1-19-69
DPL/es

w = exhaust gas flow rate, lb/sec,

ΔP = pressure drop through vent line, lb/FT^2

D = vent line diameter, FT,

A vent (0.025-inch diameter) exhausting gas at the rate of 100 cc/min. will require 3.3, 6.6, and 9.9 feet of line to promote chamber pressures of 100, 200, and 300 torr, respectively. This appears to be an excessive amount of tubing for such a small diameter. It can be incorporated into the design only by increasing the FID chamber dimensions. A chamber with a 1-inch inside diameter will require approximately 1.5, 1, and 0.5 inches of stacked coils to produce a chamber pressure of 100, 200, and 300 torr, respectively.

An alternate method of providing the flow restriction is that which utilizes a porous metal plate as one side or end of the chamber. This type of restrictor has the definite advantage of providing a more uniform flow path over a relatively wide area.

Heat losses will increase by 0.00114 W/$^{\circ}$F above the environmental temperature or approximately 0.75 W when the chamber temperature is 126° F and the environmental temperature is -40° F. Figure 5 illustrates the thermal characteristics of this detector.

FIGURE 5

FID CHAMBER THERMAL TIME RATE

OF RESPONSE CHARACTERISTICS

FID CONDUCTANCE TO ENVIRONMENT - 0.2 BTU/HR-°F
FID UNIT WEIGHT - 0.14 LBS
TEMPERATURE LEVEL PROPORTIONAL TO ENVIRONMENTAL TEMPERATURE
ENVIRONMENTAL TEMPERATURE ~ -40°F
STEADY STATE POWER REQUIRED = 0.059 w/°F

HEATING TIME ~ MINUTES

1-19-69
DPL/es
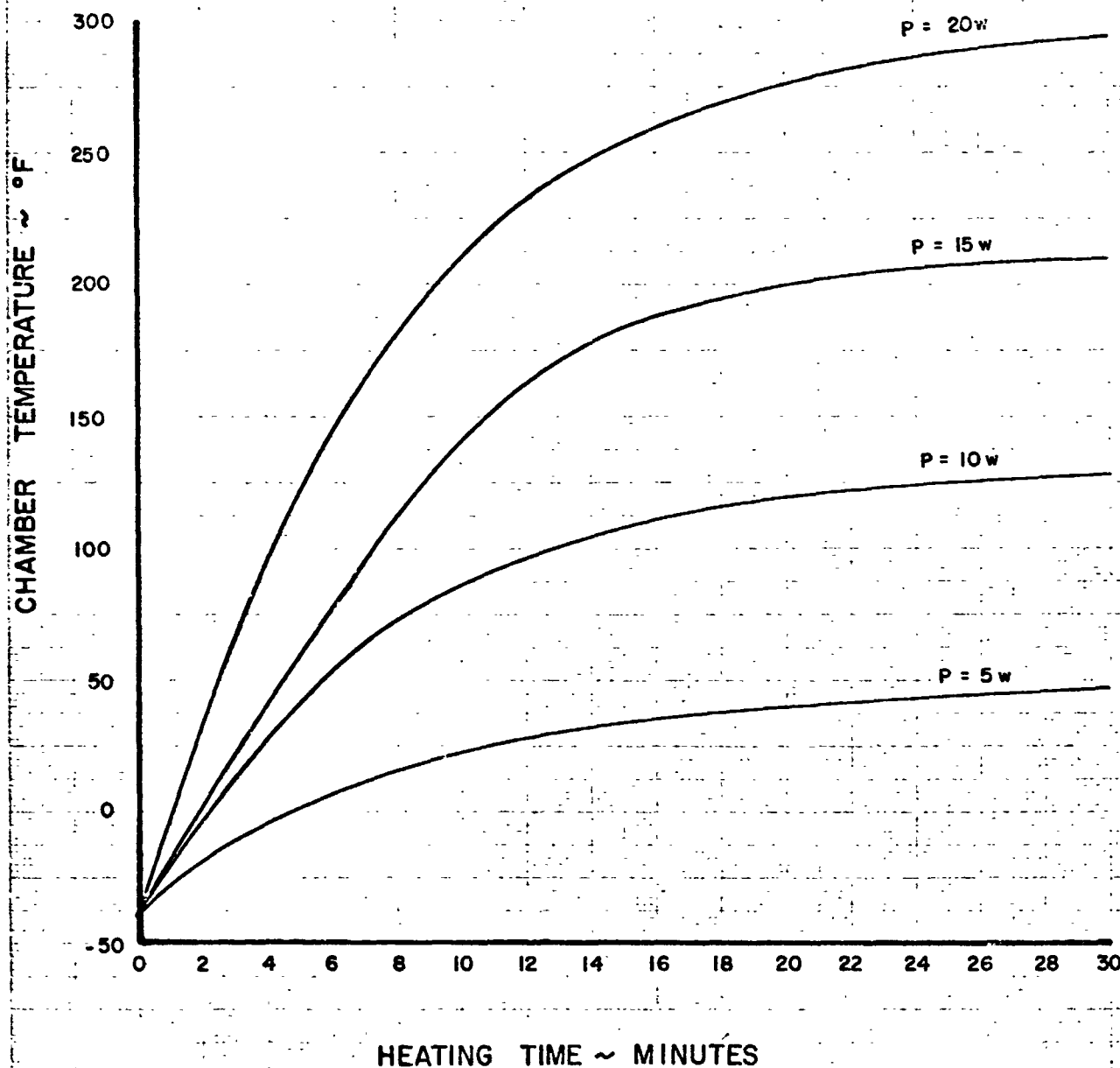
VI. PRE-PROTOTYPE DETECTOR AND TESTS
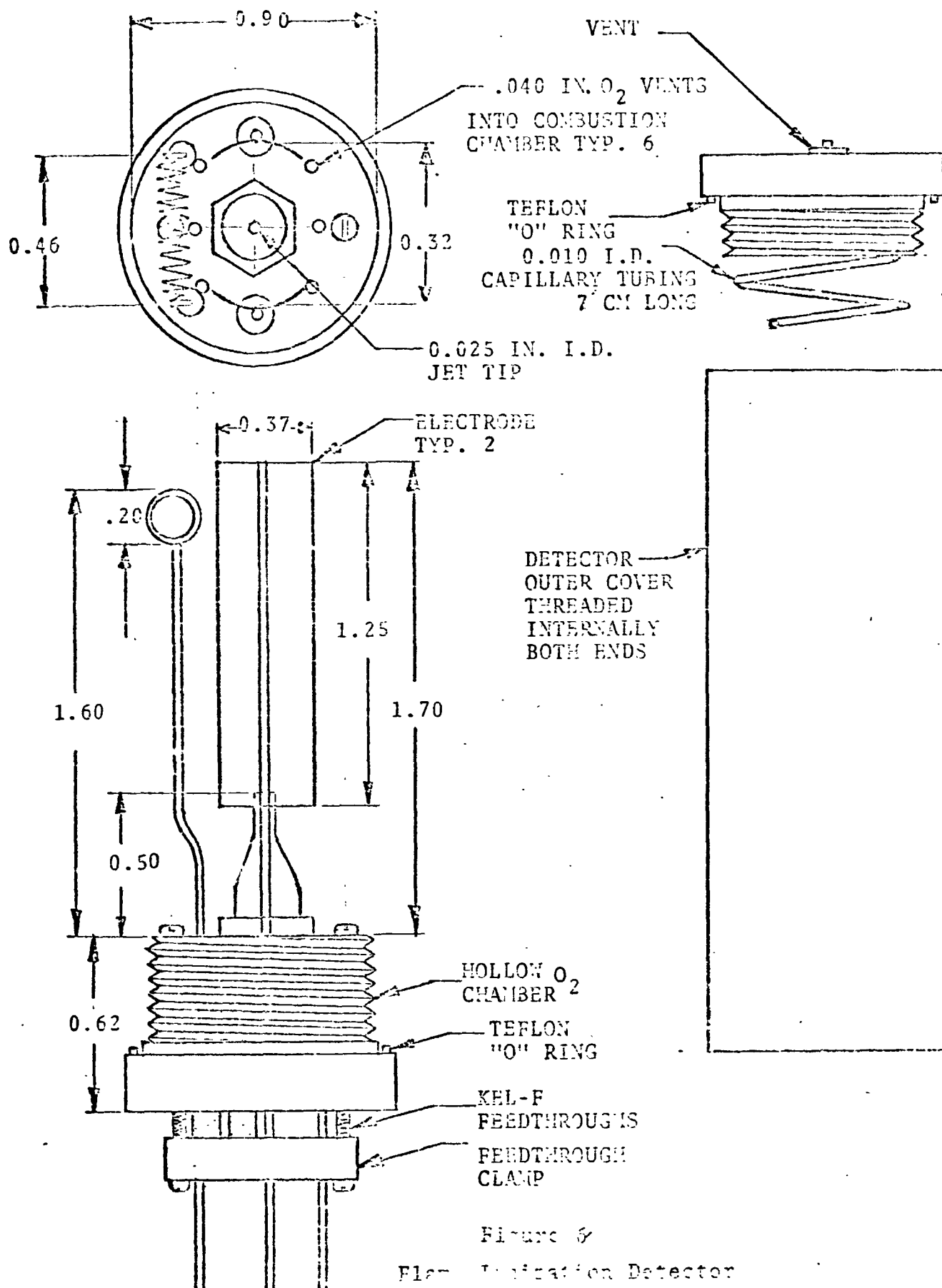
ATC DETECTOR DESCRIPTION

The pre-prototype detector was fabricated primarily
from aluminum with teflon or KEL-F seals at the mechanical
interfaces.

Figure 6 is a sketch of the detector and Figures 7
and 8 are photographs of the unit used in this study. The
detector has two curved-plate electrodes. The hot wire
ignitor is placed near the wall about 1 inch above the jet
tip. All electrical connections and both gas connections
are routed through the base of the detector. The oxygen
inlet terminates as it enters the base. The oxygen is then
dumped into a chamber below the base, which is ringed with
holes to allow the oxygen to diffuse upward and around the
jet tip.

The detector's top cap is removable and has a 7-cm,
0.010-inch capillary restrictor venting the gases to the
atmosphere. The pressure drop across the restrictor is
about 0.7 atmospheres at environmental vacuum.

A number of compromises were necessary in the detector
design because the schedule did not permit the incorporation
of long-lead items or processes. The compromises that were
made did not adversely affect the principal goal of operating
the detector under pressure, but should be avoided in future
models. The following are the recommended changes:

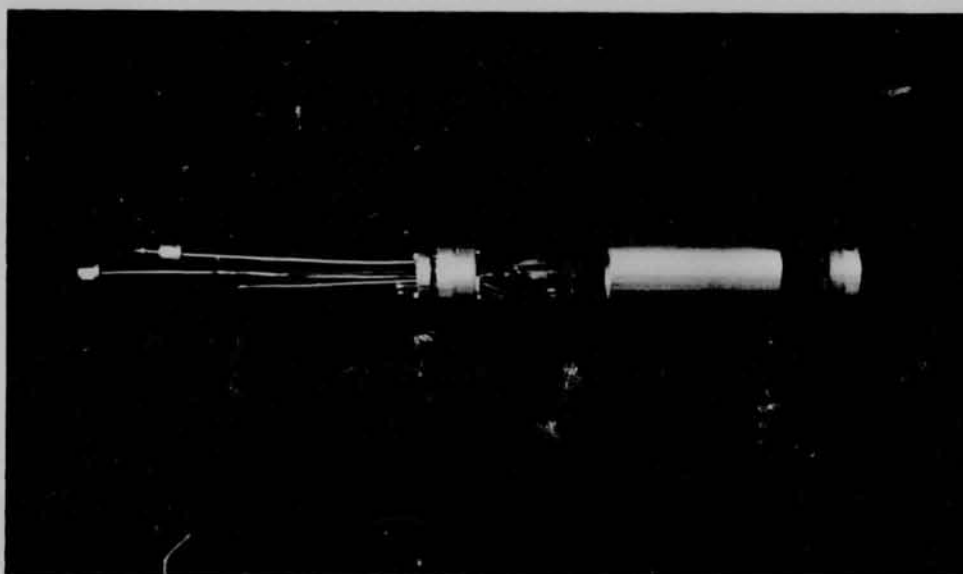1. Glass headers for electrical and gas connections.

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0.90

.040 IN. O_2 VENTS
INTO COMBUSTION
CHAMBER TYP. 6

VENT

0.46

0.32

TEFLON
"O" RING
0.010 I.D.
CAPILLARY TUBING
7 CM LONG

0.025 IN. I.D.
JET TIP

0.37

ELECTRODE
TYP. 2

.20

DETECTOR
OUTER COVER
THREADED
INTERNALLY
BOTH ENDS

1.25

1.60

1.70

0.50

HOLLOW O_2
CHAMBER

TEFLON
"O" RING

0.62

KEL-F
FEEDTHROUGHS

FEEDTHROUGH
CLAMP

Figure 6

Flame Ionization Detector

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Figure 7   Pre-Prototype Detector Disassembled

Figure 8   Pre-Prototype Detector Installed for Testing

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2. Plated or anodized aluminum.
3. Insulated jet tips.
4. Porous metal vent.
5. Replaceable jet tips.
6. Replaceable electrodes.

DETECTOR TEST SUMMARY

The following is a brief summary of results of tests
conducted on the pre-prototype detector. Figures 9 and 10
are photographs of the detector vacuum test setup. The
principal problem during the testing was the maintenance
of leak-tight mechanical interfaces.

A. Sensitivity

At 760 torr (1 atmosphere) environmental pressure
and temperature stabilized at 153° C at top of
detector and 120° C at bottom of detector after
5 minutes of operation, the sensitivity measured
was

$$0.17 \ \frac{C}{\text{g-atm C}}$$

B. Internal Ignition Pressure at Environmental Pressure
of 1 Earth Atmosphere

At vent-cap temerature of 160° C (attained after
5 minutes of operation), detector ignited and sus-
tained flame for internal pressure of 2.3 atmos-
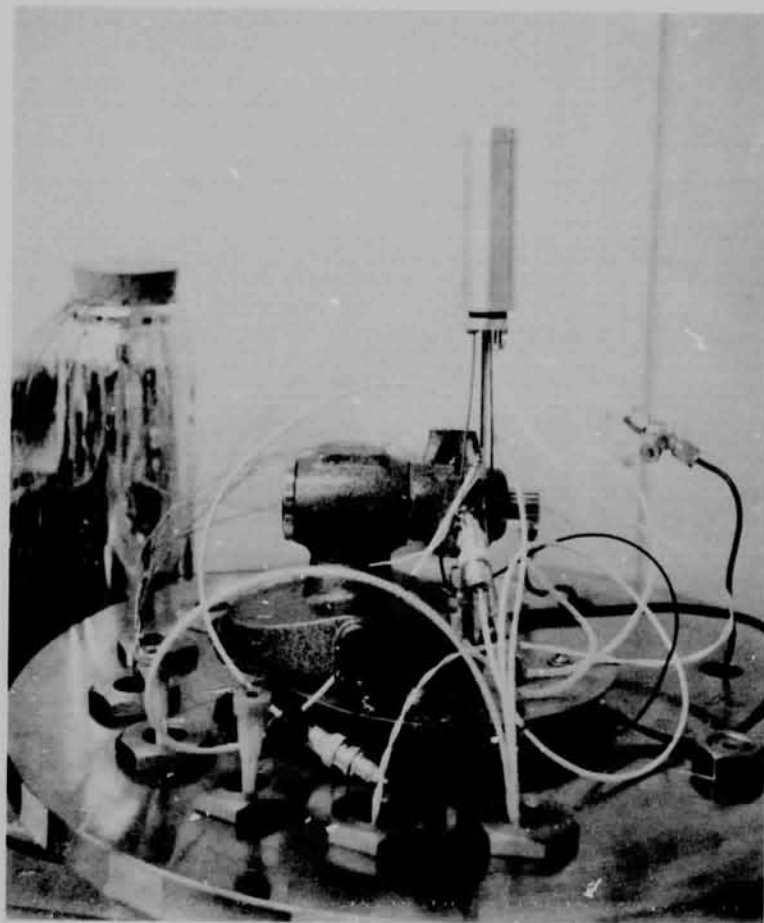pheres or greater.

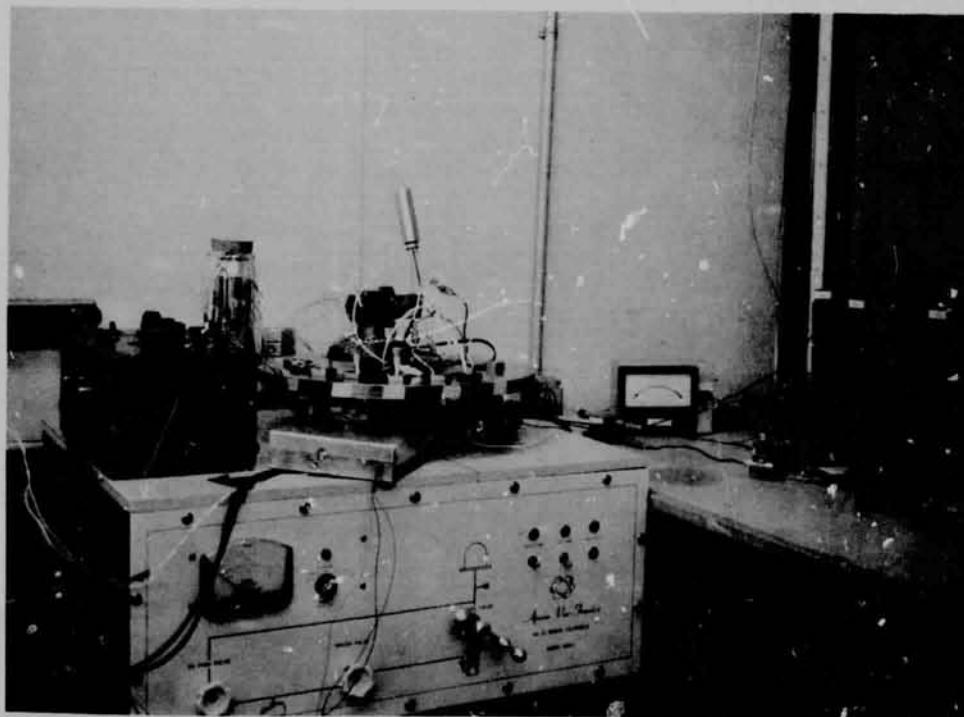Figure 9   Pre-Prototype Detector in Vacuum Test Fixture

Figure 10   Pre-Prototype Detector Vacuum Test Installation

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C. Ignition Threshold Under Varying Environmental
    Pressure

1. At 400-torr internal pressure and vent-cap
    temperature of 130° C, detector ignited at
    pressures down to 200 torr and sustained
    flame down to pressures as low as 3 torr.

2. At 400-torr internal pressure and vent-cap
    temperature of 170° C, detector ignited and
    sustained flame at pressures as low as 3 torr.

VII. GAS SYSTEM AND PYROLYSIS STUDIES

The gas-handling and pneumatic system, the sample
injection system, and the pyrolyzer were examined only
briefly before it became apparent that an extremely
thorough investigation of the flame ionization detector
deserved to be given priority. Several means for
supplying gases and injecting samples into the pyrolyzer
were studied, and the results are described here.

The first method considered for supplying gases was
a self-generating system where water is either electrolyzed
or some chemically active compound, such as lithium hydro-
xide, is added. In this manner, hydrogen and oxygen gases
are produced within the system, and savings in weight of
pressure vessels, valves, and gas conduits result. How-
ever, two primary design problems related to the continual
production of gases and the achievement of high pressures
are associated with self-generating systems. Nevertheless,
it appears that the pressure of the gases produced could
be sufficiently high, if the detector system is operated
at reduced pressures. If helium or some other diluent
gas is required, it will probably be stored and mixed into
the self-generated gases.

A second means of providing gases is to carry a
combustible mixture with the detector system and feed
it directly into the flame detector. This system, however,
has the disadvantages of a high explosion hazard and a
detector operating with a premixed flame.

Gases can also be furnished by carrying the hydrogen
and oxygen separately in supply tanks and feeding them
into the hydrogen flame detector. Optimum hydrogen and
oxygen flow rates and delivery pressures can easily be
achieved with valves, regulators, and a mixing chamber.
This, of course, is accomplished at the expense of a weight
penalty.

Several means of injecting a sample into the pyrolyzer
were also investigated. A device comprised of a helical
rotating screw enclosed by a cylindrical sleeve appears to
be adequate. It processes and transports the soil to the
pyrolyzer and indicates when it is filled. The major
problems associated with it are jamming of the screw and
integration with the pyrolyzer.

An integrated pneumatic sample acquisition and sample
injection system was also examined. Although its mechanical
moving parts were reduced to those concerned only with
deployment and alignment, it seriously limited the acquisi-
tion of surface layer samples consisting only of fine dust.
A relatively large pressurized gas supply with the attendant
penumatic system and controls is also required.

The requirements of the pyrolysis chamber were investi-
gated to help define the number of analyses to be conducted,
the average size of the soil sample and the chamber design
and configuration. Sample injection indicators, chamber
sealing methods, and chamber heating techniques were con-
ceived and preliminary calculations were made to establish
their feasibility and performance characteristics.

VIII. CONCLUSIONS

This study has resulted in the unification of hydrogen flame ionization detector technology and the fabricatio. of a pre-prototype detector which ignites and sustain a flame in a vacuum. Its sensitivity is equivalent to the best commercial detectors availabl. and ignition characteristics are superior.

The detector, however, is not ready to be utilized for carbon analysis in the Mars Lander. Detector operation in a pressurized chamber imparts undesirable characteristics associated with flame noise and stability due to internal aerodynamic disturbances and water condensation.

The stud, has established with a reasonable degree of certainty the fundamental changes which must be made to the detector and its elements: the jet tip, the electrodes, gas delivery modes, and the internal aerodynamic design. In addition, the study has permitted the definition of a preliminary design and the technical problems underlying the development of a spaceworthy prototype flight detector.

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